Standard Operating Procedure for Dissolved Organic Carbon

LG211

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1.0 SCOPE AND APPLICATION

1.1 This procedure describes the analysis of lake waters samples for dissolved organic carbon (DOC). The analysis is conducted by the initial removal of Inorganic carbon from samples followed by the conversion of all organic carbon into CO_2 by ultraviolet digestor and finally detection of carbon by infra-red (IR) analyzer.

2.0 SAFETY AND WASTE HANDLING

2.1 Refer to GLNPO's *Health, Safety and Environmental Compliance Manual* (May 1997, or as amended) and individual instrument procedural operations manuals for specific details on applicable 1) personal health and safety issues; 2) instrumental, chemical, and waste handling procedures; and 3) accident prevention. This applies to all EPA personnel, EPA contractors or federal, state, or local government agencies, and persons who operate or are passengers onboard US EPA GLNPO vessels during all activities and surveys.

2.2 All containers storing reagents, standards, controls, blanks, and wastes used in the laboratory must be properly identified through appropriate labeling and hazard definition.

2.3 Every chemical should be regarded as a potential health hazard and exposure to these compounds should be as low as reasonably achievable. Please refer to Appendix L in GLNPO's *Health, Safety and Environmental Compliance Manual* (May 1997, or as amended) for more detailed descriptions of the potential risks associated with any chemicals used in this method. It is good laboratory practice to wear a lab coat, safety goggles and gloves at all times.

2.4 It is the responsibility of the user of this method to comply with relevant chemical disposal and waste regulations as sited in GLNPO's *Health, Safety and Environmental Compliance Manual* (May 1997, or as amended). All applicable safety and waste handling rules are to be followed. Good technique includes minimizing contaminated waste.

2.5 Over-board discharges of chemical wastes are forbidden.

3.0 SUMMARY OF PROCEDURE

3.1 The determination of organic carbon requires the removal of inorganic carbon which is present in samples as carbonate. This automated pre-treatment system is designed to remove inorganic carbon by acidifying the sample. A high velocity stream of organic free air transforms the acidified sample into a thin turbulent liquid film which is transported rapidly through a large-bore coil providing the necessary surface area for efficient CO_2 removal. At a purge rate of 500 mL per minute, up to 500 mg of inorganic carbon can be removed with minimal loss of volatiles. An aliquot of the carbonate-free sample is then segmented and presented for analysis. The aliquot is mixed with a stream of acid and potassium persulfate and subjected to UV radiation. The resultant CO_2 generated from the organic carbon present in the sample is then purged with a stream of CO_2 free air or nitrogen to be measured with a non-dispersive infra-red analyzer. The electronic information is sent to a chart recorder. By measuring peaks height from the chart recorder the concentration of dissolved organic carbon is calculated.

4.0 DESCRIPTION OF INSTRUMENTATION

4.1 The instrumentation set-up for DOC is comprised of a Technicon Auto Analyzer II system (consisting of Auto Sampler IV, Proportioning Pump III, DOC manifold), ultraviolet digester, CO_2 non-dispersive IR analyzer (Beckman Model 865), source of CO_2-free air with flow control and indicators, strip chart recorder.

5.0 PREPARATION

5.1 Sample Handling and Preservation

5.1.1 Samples are filtered immediately after collection, retained in clean glass containers and stored at 4°C. Samples are stable for 24 hours.

5.2 Interferences

5.2.1 Inorganic carbon is the only substance known to interfere with DOC analysis. Inorganic carbon is removed in the initial stages of the procedure. Low results may be obtained for samples containing highly volatile organic compounds.

5.2.2 Organic vapors in chemistry laboratories, and especially refrigerators, may cause contamination of the samples unless care is taken.

5.3 Reagents and Standards

USE REAGENT WATER FOR ALL SOLUTIONS

5.3.1 All reagents should be stored in the appropriate glass bottles and labeled with the following information:

Identity:	1.0 N Sulfuric acid
Date:	mm/dd/yy
Initials of Preparer:	SAS
Concentration:	1,000 mg-C/L

All standards should be stored in the appropriate glass bottles and labeled as above.

5.3.2 **1.0 N Sulfuric acid:** Add 28 mL of concentrated sulfuric acid to about 800 mL of reagent water. Mix and dilute to one liter.

5.3.3 **4% Persulfate reagent:** Dissolve 40 g potassium persulfate ($K_2S_2O_8$) in reagent water to make one liter.

5.4 Preparation of Calibration Standards

5.4.1 **Stock 1000 mg/L Carbon Solution:** Dissolve 2.125 g potassium biphthalate ($KHC_8H_4O_4$) in 500 mL of reagent water. Add 1 mL of concentrated sulfuric acid (H_2SO_4) and dilute to one liter.

5.4.2 **Working Calibration Standards:** Prepare standards over the range of analysis. For the working range of 0.0 - 10.0 mg-C/L, the following standards may be used:

mL of stock standard solution (5.4.1) diluted to 200 mL	**Concentration mg-C/L**

2.0	10.0
1.0	5.0
0.5	2.5
0.2	1.0
0.1	0.5
0.0	0.0

Working Calibration Standards should be prepared daily.

5.4.3 Stock 514 mg/L C Control Standard: Dissolve 1.2604 g of glutamic acid ($C_5H_9O_4N$), dried for 2 - 3 hours at 70°C, in 500 mL of reagent water. Add 1 mL of concentrated sulfuric acid (H_2SO_4) and dilute to one liter.

5.4.4 **Working Control Standards:**

QC Type	mL of stock control standard solution (5.4.3) diluted to 200 mL	Concentration mg-C/L
High Check (CS-1)	2.0	5.14
Low Check (CS-2)	0.5	1.28

Working Control Standards should be prepared daily.

6.0 ANALYTICAL PROCEDURE

6.1 Instrument Set-up

6.1.1 Connect all the different parts of instrument as per manifold diagram on page 9. Make sure there are no leaks in the air system. Activate the IR analyzer by turning on the main switch and allowing it to warm up for a minimum of 2 hours prior to use. At the same time have CO_2-free air flow through the detector and set the meter to read near zero with zero control. After setting up the complete analytical system as described in the DOC manifold diagram, switch on the reagents, gas flow, the UV digestor and proportioning pump and wait for a stable baseline before starting an actual run.

6.2 Procedure

6.2.1 Before starting an analysis run the highest calibration standard (primer) to adjust the peak height on the chart recorder.

6.2.2 The Calibration and Check Standard results are to be evaluated based upon criteria set in Section 9.0.

6.2.3 Once a stable baseline is achieved, calibration, check standards and samples are run on the system as per the wheel pattern described below.

Primer

10.0

5.0

2.5

1.0

0.5

0.0

R. BLK

CS-1

CS-2

40
Samples

R. BLK

CS-1

CS-2

6.3 Instrument Shut-down

6.3.1 After a shift is completed, the system is to be shut-down. First, put the system on wash for at least 30 minutes. Then turn off sampler, proportioning pump, and UV digestor. The organic-free air supply should be allowed to run through the IR detector.

6.3.2 **The IR analyzer should not be turned off.**

7.0 CALCULATIONS

7.1 Measure the peak heights of the calibration standards (manually or by computer).

7.2 Calculate the regression equation using a second-order regression with zero forcing. Apply this regression equation to determine the DOC concentration.

8.0 MAINTENANCE AND TROUBLE-SHOOTING

8.1 An unstable baseline may indicate that system needs retubing or there is a leak in the air system.

8.2 Change Drierite trap between the phase separator and the IR detector prior to complete exhaustion.

9.0 QUALITY CONTROL

9.1 The minimum acceptable correlation coefficient (r) for calibration curve 0.995.

9.2 The following QC samples must be prepared and analyzed at the minimum frequency indicated.

QC Sample Type		Frequency	Acceptance Criteria
External	Field Reagent Blank (FRB)	One per basin[a]	0.00 ± 0.60 mg/L or less than one tenth associated field sample concentrations, whichever

			is greater
	Lab Duplicate (LD1)	One per basin[a]	RPD ≤ 20%
Internal	Calibration	At the beginning of each batch	r ≤ 0.995
	High Check Standard (CH)	At the beginning & end of each batch or 1 per 40 samples, whichever is more frequent	5.14 ± 0.90 mg/L
	Low Check Standard (CL)	At the beginning & end of each batch or 1 per 40 samples, whichever is more frequent	1.28 ± 0.60 mg/L
	Laboratory Reagent Blank (LRB)	At the beginning & end of each batch or 1 per 40 samples, whichever is more frequent	0.00 ± 0.60 mg/L
	Method Detection Limit (MDL)	Once per year and each time a significant change is made to the SOP	not specified

[a] A field duplicate, lab duplicate, and field reagent blank are collected with each group of 3, 4, or 5 stations depending on the lake. A Random Number Generator (RNG) is used to determine the stations and depths of these QC samples. Where basins are well defined, at least one of each is collected from each basin.

9.3 Assessment

9.3.1 The analyst must compare analytical results to the acceptance criteria listed in Section 9.2 to identify QC failures. If the results are outside the acceptance criteria, the analyst should first review their calculations for errors and if none are identified, they must follow the corrective action procedures listed in Section 9.4.

9.4 Corrective Actions

9.4.1 Corrective action procedures will often be handled at the bench level by the analyst, who reviews the preparation or extraction procedure for possible errors, checks the instrument calibration, spike and calibration mixes, instrument sensitivity, and any other potential sources of error. If failure occurs and an error is identified, the analyst should re-run quality control and RFS samples in the entire analytical batch to confirm the results. Because external QC samples are collected and prepared during the survey and provided to the contractor or grantee laboratory, a single rerun to confirm results is sufficient when all other QC samples are within acceptance criteria. For analyses conducted onboard, if the problem persists or cannot be identified, the matter must be referred to the Chief Scientist for further investigation. Depending upon the Chief Scientist's evaluation, the analyst may or may not be required to prepare and re-run the samples again. Additionally, if the results are significantly different than the expected concentrations based on historical data or related samples, then the analyst may split the RFS sample in the laboratory and analyze the splits. Once a decision is made, full documentation of the corrective action procedures and assessment of the final result must be filed with the WQS QM Technical Lead (Marvin Palmer) or the GLNPO QM. For analyses conducted at contract or grantee laboratories, this information can be included with submitted data. When contractor or grantee laboratories have a question regarding acceptable corrective actions, they should contact the Biology Technical Lead or Limnology Technical Lead as appropriate for instruction at a time when corrective action can still be taken.

9.5 Data Reporting/Recording

9.5.1 When corrective actions are not feasible or do not resolve QC failure, the analyst is responsible for identifying all failed QC samples and RFS samples. If analyses are being conducted onboard, the analyst

should document the QC information on the hard-copy Field Information Recording Forms (Appendix H). If analyses are being conducted by contract or grantee laboratories, the analyst should document all QC information with the submitted data.

10.0 REFERENCES

10.1 Technicon Method #451-76W. Technicon Industrial Systems, Tarrytown, New York, 10591.

10.2 Operation Manual for Infrared analyzers, Models 215b, 315b, and 415b. Beckman Instruments, Inc. Fullerton, CA 926

11.0 DISSOLVED ORGANIC CARBON MANIFOLD DIAGRAM

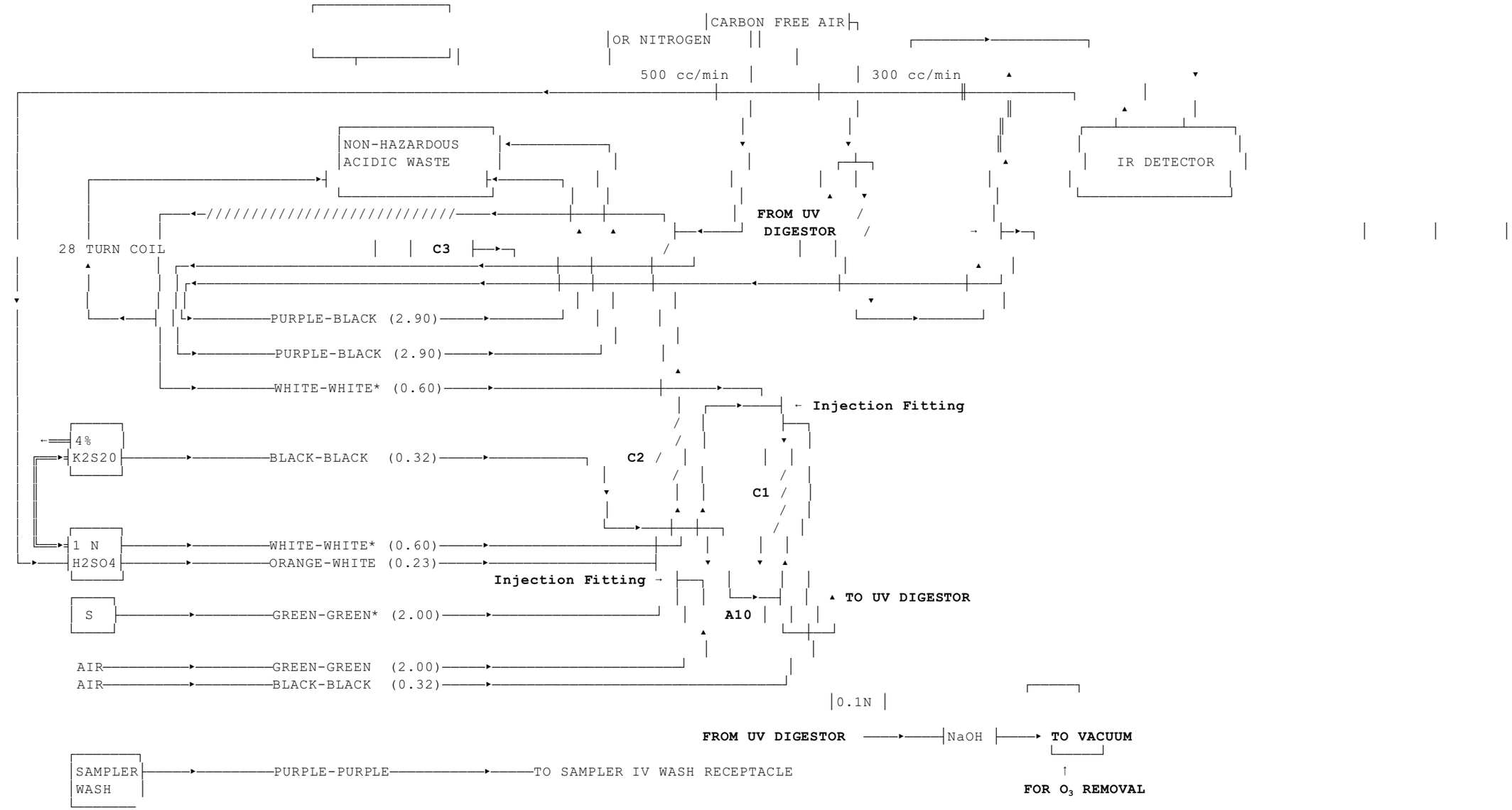

DIAGRAM LEGEND: - Injection Fitting (116-0489-01), **C1** - 5 turn coil (170-0103), **C2** - 20 turn coil (157-0248), **C3** - Glass Fitting (116-0202), **C4** - 20 turn coil (116-0127-06), **A10** - Glass Fitting (116-B034), **S** - Sampler IV 20/hr 1:1, ***** - Silicon Tube